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Momentum distribution of non-hydrogenic electrons

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Abstract : The momentum distribution of the valence electrons of ^{3}Li, ^{11}Na and ^{19}K is studied by using non-hydrogenic wave functions of the quantum-defect theory. The results obtained are compared with those produced by the self-consistent-field functions It is shown that the non-hydrogenic electrons have in general, a high momentum component as compared to the prediction of the Hartree-Fock theory.

Keywords : Quantum defect theory, wavefunction, momentum distribution

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The momentum distribution of electrons in an atom provides valuable information about the properties of the system [1]. It is also used for the interpretation of positron annihilation experiment [2], and for the calculation of inner-shell ionization cross sections by charged particle impact in the binary counter or classical approximations [3]. The electron momentum distribution (EMD) is expressed in terms of the momentum space wave function obtained by Fourier transforming the corresponding radial space function. Studies in EMD have a rather old root in the quantum literature [4] and are often envisaged in response to need of different physical applications [5]. We believe that for many-electron atoms similar investigations have yet remained an interesting curiosity presumably because a many-body problem in physics is, in general, not exactly solvable. Thus over the years, the N-electron problem has been discussed and treated within the framework of various approximation schemes [6]. While the general many-electron problem is still largely unsolved, the structure and spectra of alkali-metal atoms can be understood relatively simply because they are made up of closed shells with one valence electron. Sommerfeld [7] assumed that the valence electron of these atoms can be excited easily leaving the other electrons in a much more tightly bound core. The excited electron may be regarded to move in a potential due to the nucleus and to the core electrons, and spend much of its time in an outer region where the nucleus is screened by the core electrons and where the potential is of Coulomb form, and some fraction of its time penetrating the region of the core. In this region there is a stronger attractive potential which causes the orbit to precess. Since there is no precession of the closed elliptical orbits in a pure Coulomb potential, we shall call the valence electrons of alkali-metal atoms as non-hydrogenic. The object of the present work is to study the momentum distribution of these electrons by using a judicious physical model provided by the so called the quantum defect theory (QDT) [8].

In the QDT, the energy spectrum of a non-hydrogenic electron is still accounted for by a hydrogenic formula but with the principal quantum number n replaced by an effective quantum number ν and the quantum defect μ is defined by

$$\mu = n - \nu. \tag{1}$$

The quantity μ is traditionally obtained by fitting the experimental binding energy. The concept of a half-empirical quantum defect method was introduced in the early works on quantum mechanics and played a significant role in spectroscopic studies. During the last few decades, Seaton, Fano and others [8,9] carried out extensive studies on this quantum defect method and gave it a more mature status, currently known as the QDT. An interesting aspect of the QDT is that the value of the quantum defect determines not

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only the energy of the state but also the spatial character of the wave function. For example, the hydrogenic wave functions are expressed in terms of the confluent hypergeometric or regular Whittaker functions. In contrary to this, the non-hydrogenic wave functions of the QDT requires the irregular Whittaker functions for their description [10]. In this work, we shall compare the momentum distribution of non-hydrogenic electrons of some alkali-metal atoms with that produced by the self-consistent-field functions which represent the best wave functions for many-electron atoms in the sense of the variational principle [11]. For the present purpose we shall make use of the analytical Hartree-Fock-Roothaan (HFR) wave functions as tabulated by Clementi and Roetti [12]. The use of these wave functions on the one hand, provides a lot of calculational simplicity and, on the other hand, gives results as accurate as those obtained by the numeric Hartree-Fock wave functions.

The non-hydrogenic wave function due to Seaton [8] is given by

$$P_{nl}(r) = \left[\chi(\nu)\nu^2\Gamma(\nu+l+1)\Gamma(\nu-l)\right]^{-\frac{1}{2}} \times W_{\nu,l+\frac{1}{2}}\left(\frac{2r}{\nu}\right), \tag{2}$$

where $W_{\nu,\frac{1}{2}}(.)$ stands for the irregular Whittaker function and

$$\chi(\nu) = 1 - \frac{2}{\nu^3}\frac{d\mu(\varepsilon)}{d\varepsilon}. \tag{3}$$

Here, ε is the energy parameter and l, the angular momentum of the atomic electron. In writing (2) we have employed the Hartree atomic units. Recently, Chaudhuri *et al* [13] derived a closed form analytic expression for the Fourier transform of (2). Since the valence electrons of alkali metal atoms are s electrons we quote below only the result for $l = 0$. The momentum space wave function of our interest is given by

$$g_{\nu 0}(q) = \left[\frac{2}{\pi\nu}\right]^{\frac{1}{2}} \frac{4\nu}{(1+q^2\nu^2)^2} C_{\nu 0}(\zeta), \tag{4}$$

where

$$C_{\nu 0}(\zeta) = \frac{\nu\sin[\nu(\theta-\pi)]}{\sin(\theta-\pi)} + \frac{\sin(\nu\pi)}{\pi}\left[\frac{-1}{2(1-\zeta)} + \frac{z}{(z^2-1)} \times \left\{{}_2F_1(1,\nu;1+\nu;z) - {}_2F_1\left(1,\nu;1+\nu;\frac{1}{z}\right)\right\}\right] \tag{5}$$

with $$2\zeta = x = z + z^{-1} \equiv \frac{q\nu-i}{q\nu+i} + \frac{q\nu+i}{q\nu-i} \tag{6}$$

and $$\theta = \arccos\left\{\frac{(q^2\nu^2-1)}{(q^2\nu^2+1)}\right\}. \tag{7}$$

The HFR type wave functions for the orbital i as tabulated by Clementi and Roetti [12] for alkali-atom ground states are written as

$$\phi_i(r) = \sum_j C_{ij}\chi_j(r), \tag{8}$$

where C_{ij} are expansion coefficients and the basis functions $\chi_j(r)$ are defined by

$$\chi_j(r) = \left[(2n_j)!\right]^{-\frac{1}{2}}(2\xi_j)^{n_j+\frac{1}{2}} r^{n_j}\exp(-\xi_j r). \tag{9}$$

In (8), the j-sum extends over a small finite number of basis functions. The quantities n_j and ξ_j are the appropriate principal quantum number and orbital exponent of $\chi_j(r)$, respectively. The momentum space wave function corresponding to (8) can be obtained in a rather routine fashion to read

$$\phi_i(q) = \sqrt{\frac{2}{\pi}}\sum_j C_{ij}\left[(2n_j)!\right]^{-\frac{1}{2}} 2^{n_j+\frac{1}{2}}\xi_j^{2n_j+\frac{1}{2}} \times \frac{\Gamma(n_j+2)}{\left(\xi_j^2+q^2\right)^{n_j+1}} {}_2F_1\left[\frac{-n_j}{2}, \frac{-n_j+1}{2}; \frac{3}{2}; \frac{-q^2}{\xi_j^2}\right] \tag{10}$$

In terms of q-space wave function $\psi(q)$, the momentum distribution $P(q)q^2$ is given by

$$P(q)q^2dq = |\psi(q)|^2 q^2 dq. \tag{11}$$

We shall call this distribution as d_1 when $\psi(q)$ refers to the non-hydrogenic wave function in (4). Similarly, d_2 will stand for the momentum distribution calculated by using the wavefunction in (10). In the following, we shall compare the results for d_1 and d_2 and try to gain some physical meaning for the non-hydrogenic nature of the valence electrons of alkali-metal atoms.

Using the values for quantum defect μLi = 0.4115, μNa = 1.3729 and μK = 2.2295 for the ground state of valence electrons [14] and the parameters of the HFR wave function [12], we have compared values for d_1 and d_2. In Figures 1–3, we display these results for the valence electrons of alkali-metal atoms, ^{3}Li, ^{11}Na and ^{19}K respectively. A common feature of these plots is that the QDT distribution d_1 and HFR distribution d_2 do not differ appreciably. In particular for ^{3}Li, the two sets of data for d_1 and d_2 are not discernible on the plot used by us. Some difference, however, tends to show up as we go to higher alkalies. Looking closely into Figure 2, we see that the prominent peak of d_1 falls slightly below that of d_2 and is pushed towards the higher momentum. A similar deviation between the two curves becomes more significant in the case of Potassium (Figure 3) such that pushing off of the first peak results in an augmented value for the second peak of d_1 relative to that

of d_2. This indicates that the non-hydrogenic electrons of the QDT have a large high-momentum component as compared to the HFR ones. Alternatively, in the quantum-defect theoretic description, we regard the valence electrons of alkali metal atoms to move in a more attractive environment than the potential simulated by the self-consistent-field model. From the physical view point, the QDT is believed to take better account of exchange and correlation effects of the orbital electrons than is possible in a simple potential representation of the interaction as in the HFR description [14].

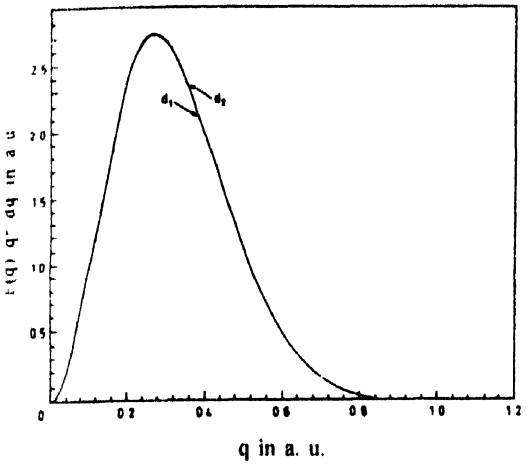

Figure 1. Momentum distribution of the valence electron of ^{3}Li as a function of the momentum q. The solid line gives the distribution (d_1) due to the non-hydrogenic wave function (4) and the broken line (not discernible) gives a similar result for (d_2) due to Hartree-Fock representation (10) of the atomic electron.

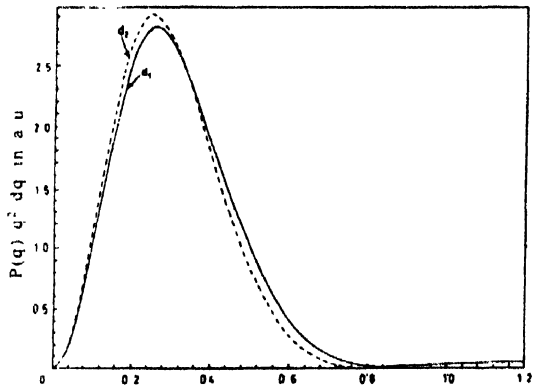

Figure 2. Momentum distribution of the valence electron of ^{11}Na. The solid and broken lines represent the variation of d_1 and d_2 as in Figure 1

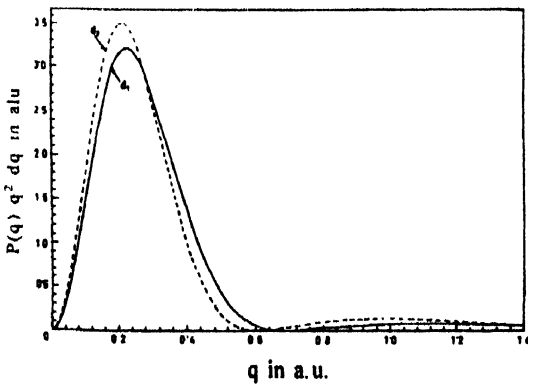

Figure 3. Momentum distribution of the valence of ^{19}K. The solid and broken curves have the same meaning as in Figure 2.

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